The Reaction of Cholest-4-en-3β-ol (Allocholesterol) with the Dichlorobis(triphenylphosphine)platinum(II)-Stannous Chloride Complex

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Recently it has been reported that a noble metal complex acts as an efficient selective catalyst in the homogeneous hydrogenation of some steroids.[1] We now wish to report a new fact observed in the hydrogenation of steroids containing an allylic alcohol system with a dichlorobis(triphenylphosphine)platinum(II)-stannous chloride hydrate complex.[2]

Cholest-4-en-3β-ol (allocholesterol) (I) gave 5α-cholest-3-ene (II) and $\Delta^{2,4}$-cholestadiene (III) upon treatment with the complex at room temperature under a hydrogen pressure of 30 kg/cm² in a benzene-methanol (vol. ratio 3 : 2) solution. 5α-Cholestan-3β-ol (IV) was found in a very poor yield after a prolonged reaction, and no 5α-cholestane (V) was isolated. The results of reactions under various conditions are summarized in Table 1.

II was obtained in the maximum yield of 46.6% when the co-catalyst was used in a molar ratio to the catalyst of ten to one; this agrees with the finding reported by Tayim and Bailar.[3] When the reaction was carried out without stannous chloride, only cholest-4-en-3-one (VI) was yielded in spite of the presence of molecular hydrogen. Also accompanied by a small amount of a hydrogenolysis product, cholest-4-ene (VII), VI was afforded through the reaction performed in benzene as the only solvent. It is worthy of note that I was converted to II and III, but not to VI, by the reaction carried out under a nitrogen instead of a hydrogen atmosphere.

These experimental data have a strong resemblance to the results of the formation of acrolein from allyl alcohol or of *cis*-2-butene, butadiene and methyl vinyl ketone from 3-hydroxy-1-butene in the reactions with the same complex system.[4]

The consumption of methanol in the reaction course was confirmed by the identification of formaldehyde (characterized as the dimedone derivative). Accordingly, it may be considered that the above-mentioned complex system was reduced to a hydrido compound with methanol; the reduced complex then acts as the reducing agent in the course of reaction I to II. Attempts to cause a reaction using isopropyl alcohol and *t*-butyl alcohol as hydrogen sources were unsuccessful. It is of interest that the stereoisomer of I, cholest-4-en-3α-ol (epiallocholesterol) (VIII), was inert to the reaction with the platinum-tin complex. The structures of the above-mentioned compounds were confirmed by means of mp, $[\alpha]_D$, IR, NMR, TLC, VPC, *etc.*

A study of the hydrogenation with a dichlorobis(trialkylphosphine)platinum(II)-stannous chloride complex is in progress and will be reported on shortly.

TABLE 1

Catalyst*	React. time (hr)	Gas pres. (kg/cm²)	Product yields (%)				Recovered I (%)
			VI	III	II	IV	
Pt only	5	H_2 30	6.3	0	0	0	92.8
Pt:Sn=1:2	5	H_2 30	3.7	21.0	38.0	0	35.6
Pt:Sn=1:2	5	N_2 30	0	16.7	25.2	0	56.9
Pt:Sn=1:2	10	H_2 30	4.3	23.2	39.4	trace	32.5
Pt:Sn=1:3	5	H_2 30	6.5	20.0	38.6	0	33.8
Pt:Sn=1:10	5	H_2 30	7.1	20.2	46.6	2.4	23.1
Pt:Sn=1:10	10	N_2 30	0	17.6	40.8	0	41.3

* Pt indicates $PtCl_2[P(C_6H_5)_3]_2$, and Sn indicates $SnCl_2 \cdot 2H_2O$.

1) *E.g.* a) C. Djerassi and J. Gutzwiller, *J. Am. Chem. Soc.*, **88**, 4537 (1966). b) A. J. Birch and K. A. M. Walker, *Tetrahedron Letters*, **1966**, 4939. c) S. Nishimura and K. Tsuneda, This Bulletin, **42**, 852 (1969).

2) E. N. Frankel, E. A. Emken, H. Itatani and J. C. Bailar, Jr., *J. Org. Chem.*, **32**, 1447 (1967).

3) H. A. Tayim and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 3420 (1967).

4) Y. Ichinohe and N. Kameda, unpublished observations.